Comments on "State equation for the three-dimensional system of 'collapsing' hard spheres"

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A recent paper [I. Klebanov et al. *Mod. Phys. Lett. B* **22** (2008) 3153; arXiv:0712.0433] claims that the exact solution of the Percus–Yevick (PY) integral equation for a system of hard spheres plus a step potential is obtained. The aim of this paper is to show that Klebanov et al.'s result is incompatible with the PY equation since it violates two known cases: the low-density limit and the hard-sphere limit.

Keywords: Percus–Yevick equation; square-well fluids; square-shoulder fluids.

1. Introduction

Given a fluid of particles interacting via a certain potential $\phi(r)$, access to its (equilibrium) structural and thermodynamic properties is usually obtained by means of approximate integral equations,[1] whose solution typically requires hard numerical work. Exceptions are practically restricted to the Percus–Yevick (PY) equation for hard spheres[2,3] and sticky hard spheres,[4] and the mean spherical approximation (MSA) for the hard-core Yukawa potential.[5]

The simplest potential including an energy scale and two length scales is that of hard spheres plus a step-function tail:

$$\phi(r) = \begin{cases} \infty, & r < \sigma, \\ \epsilon, & \sigma < r < \lambda, \\ 0, & r > \lambda. \end{cases} \tag{1}$$

If $\epsilon < 0$, the step potential is attractive and Eq. (1) describes the well-known square-well potential. On the other hand, $\epsilon > 0$ defines the square-shoulder potential. The pure hard-sphere fluid is recovered if either $\epsilon = 0$ (at arbitrary λ/σ), or $\lambda = \sigma$ (at arbitrary, but finite, ϵ), or $\epsilon \to \infty$ (again, at arbitrary λ/σ).

Starting from the PY integral equation, Wertheim[6] was able to express the Laplace transform

$$G(t) \equiv \int_\sigma^\infty dr\, e^{-tr} r g(r), \tag{2}$$

where $g(r)$ is the radial distribution function, in terms of quantities involving the cavity function $y(r) \equiv e^{\phi(r)/k_B T} g(r)$ (where k_B is the Boltzmann constant and T

is the temperature) only in the interval $0 \le r \le \lambda$:

$$G(t) = \frac{(1+4\pi\rho K)t^{-2} - F(t) + 2\pi\rho t^{-1}\left[Y(-t) - Y(t)\right]}{1 + 2\pi\rho t^{-1}\left[F(-t) - F(t)\right]}, \tag{3}$$

where ρ is the number density, $K \equiv -F'(0)$, and

$$F(t) \equiv -\int_0^\lambda dr\, e^{-tr} r f(r) y(r), \tag{4}$$

$$Y(t) \equiv -\int_0^{\lambda-\sigma} dr\, e^{-tr} \int_{\sigma+r}^{\lambda} dr'\, r' f(r') y(r') (r - r') \left[1 + f(r - r')\right] y(r - r'). \tag{5}$$

Here, $f(r) \equiv e^{-\phi(r)/k_BT} - 1$ is the Mayer function. Equations (3)–(5) apply not only to the potential (1) but more in general to any interaction with a hard-core at $r = \sigma$ and a finite range at $r = \lambda$.

In a recent paper,[7] Klebanov et al. claim that they obtain the exact solution of the PY integral equation for the potential (1). According to their approach, Eq. (3) is complemented by

$$y(r) = C_1 + C_2 r + C_4 r^3, \quad 0 \le r \le \lambda, \tag{6}$$

where the coefficients C_1, C_2, and C_4 are the solutions of a closed set of equations. Inserting Eq. (6) into Eqs. (4) and (5), one gets $F(t)$ and $Y(t)$, and hence $G(t)$ through Eq. (3).

The aim of this paper is to show that, in contrast to what is claimed in Ref. [7], Eq. (6) is not compatible with the PY solution because it contradicts known results in the low-density limit as well as in the hard-sphere limit.

2. Low-density limit

The virial expansion of the cavity function is

$$y(r) = 1 + \sum_{n=1}^{\infty} \rho^n y_n(r), \tag{7}$$

where the functions $y_n(r)$ are represented by sums of diagrams.[1] In the special case of the potential (1), the first-order contribution $y_1(r)$ is given by[8]

$$y_1(r) = (1+\gamma)^2 \Phi_{\sigma,\sigma}(r) - 2\gamma(1+\gamma)\Phi_{\sigma,\lambda}(r) + \gamma^2 \Phi_{\lambda,\lambda}(r), \tag{8}$$

where $\gamma \equiv e^{-\epsilon/k_BT} - 1$ and

$$\begin{aligned}\Phi_{a,b}(r) \equiv{}& \frac{\pi}{12r}\left[3(a+b)^2 - 2(b-a)r - r^2\right](b-a-r)^2\Theta(b-a-r)\\ &-\frac{\pi}{12r}\left[3(b-a)^2 - 2(a+b)r - r^2\right](a+b-r)^2\Theta(a+b-r),\end{aligned} \tag{9}$$

$\Theta(x)$ being Heaviside's step function. More explicitly, in the interval $0 \le r \le 2\sigma$ one has

$$y_1(r) = (1+\gamma)^2 \frac{\pi}{12}(4\sigma + r)(2\sigma - r)^2 + \gamma^2 \frac{\pi}{12}(4\lambda + r)(2\lambda - r)^2 - 2\gamma(1+\gamma)\frac{4\pi}{3}\sigma^3$$
$$+2\gamma(1+\gamma) \times \begin{cases} 0, & 0 \le r \le \lambda - \sigma, \\ \pi \frac{3(\sigma+\lambda)^2 - 2(\lambda-\sigma)r - r^2}{12r}(\lambda - \sigma - r)^2, & \lambda - \sigma \le r \le 2\sigma. \end{cases} \quad (10)$$

We see that, while $y_1(r)$ is a cubic function in the interval $0 \le r \le \lambda - \sigma$, it is a quartic polynomial function divided by r for $r > \lambda - \sigma$. Moreover, the second derivative of $y_1(r)$ is discontinuous at $r = \lambda - \sigma$. Therefore, Eq. (6) is inconsistent with Eq. (10) to first order in density. Since the PY theory yields the exact $y_1(r)$ for any interaction potential,[1] we conclude that Eq. (6) is inconsistent with the true PY solution.

3. Hard-sphere limit

As an independent test, let us now take the limit $\epsilon \to 0$ keeping λ/σ fixed. In that case, as said above, the potential (1) reduces to that of hard spheres of diameter σ, the value of $\lambda > \sigma$ not playing any role. The exact solution of the PY equation for hard spheres is well known.[1,2,3,6] In particular, the functional form of $y(r)$ for $0 \le r \le 2\sigma$ is[2]

$$y(r) = \begin{cases} A_0 + A_1 r + A_3 r^3, & 0 \le r \le \sigma, \\ \frac{B_1}{r} e^{-\kappa_1 r} + \frac{B_2}{r} e^{-\kappa_2 r} \cos(\omega r + \varphi), & \sigma \le r \le 2\sigma, \end{cases} \quad (11)$$

where the coefficients A_i, B_i, κ_i, ω, and φ are functions of density whose explicit expressions will not be needed here. It is quite clear that Eq. (6) cannot reduce to Eq. (11) if $\epsilon \to 0$ with $\lambda > \sigma$. Therefore, Eq. (6) is again incompatible with the PY equation.

4. Conclusion

In summary, the approximation presented in Ref. [7] is not the solution of the PY integral equation for the interaction potential (1), in contrast to what is claimed by Klebanov et al. The flaw in their derivation could be due to the fact that, at a given point, the authors discard the product $G(t)F(-t)$ when manipulating Eq. (3). Therefore, what they obtain is, at most, an approximation to the true solution of the PY equation, differing from the latter even in the low-density and in the hard-sphere limits.

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References

1. J.-P. Hansen, I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 2006).
2. M. S. Wertheim, *Phys. Rev. Lett.* **10** (1963) 321–323.
3. E. Thiele, *J. Chem. Phys.* **39** (1963) 474–479.
4. R. J. Baxter, *J. Chem. Phys.* **49** (1968) 2770–2774.
5. E. Waisman, *Mol. Phys.* **25** (1973) 45–48.
6. M. S. Wertheim, *J. Math. Phys.* **5** (1964) 643–651.
7. I. Klebanov, N. Ginchitskii, and P. Gritsay, *Mod. Phys. Lett. B* **22** (2008) 3153–3157.
8. J. A. Barker and D. Henderson, *Can. J. Phys.* **45** (1967) 3959–3978.